A study on selective reduction of NOx by propane on Co-Beta

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Selective catalytic reduction of NOx by propane was investigated on Co-Beta to clarify the loaded states of cobalt and their role in catalytic activity. At low ion exchange levels less than 100%, loaded cobalt is highly dispersed, which has a high selectivity for NOx reduction. At ion exchange levels much higher than 100%, Co_3O_4 appears as identified by Raman spectroscopy, and it contributes to propane oxidation by oxygen and lowers the selectivity especially at high temperatures.

Keywords: Co-Beta, propane, NOx reduction, Raman spectroscopy, cobalt oxide

1. Introduction

Recently, with increasing global concern over air pollution caused by nitrogen oxides, mandated requirements for NOx emission control are being tightened. At present, two catalytic NOx reduction processes are practically applied. One is the three-way catalyst for stoichiometric-combustion gasoline vehicles. The other is the selective catalytic reduction by ammonia (ammonia-SCR) for stationary emission sources such as power plants. However, there is no suitable lean NOx reduction process for mobile or small-scale emission sources, such as diesel or lean-burning vehicles, and cogeneration plants, in which the application of ammonia-SCR is impractical from the viewpoint of economy and safety. Under such circumstances, selective catalytic reduction of NOx by hydrocarbons (HC-SCR) has become an object of intense research since the patent applications by Volkswagen [1] and Toyota [2] groups and the pioneering work by Iwamoto et al. [3]. HC-SCR may provide a convenient and inexpensive process for lean NOx reduction if the fuel or unburnt hydrocarbons can be used as reductants. Till now, HC-SCR using various hydrocarbons such as methane [4], propane [5,6], and ethene [5–7] are reported. However, considering the case of natural gas-fueled appliances, the only available reductants are light alkanes such as methane and propane. Moreover, from a practical viewpoint, the importance of the selectivity for NOx reduction as defined by (reduced NOx)/(consumed hydrocarbon) should be stressed, since low selectivity for NOx reduction requires a higher concentration of reductants, which means a high cost of NOx reduction. This is particularly so in the case of stationary sources such as cogeneration plants, since in these cases ammonia-SCR may be used if cost permits.

Concerning the use of light alkanes as reductants, methane-SCR on Ga or In ion-exchanged ZSM-5 [8] and Co ion-exchanged zeolites [4] are already reported. However, their activities are severely inhibited by water vapor [9,10] and are not sufficient for practical application.

The authors have already reported that Co-Beta shows both high activity and selectivity for NOx reduction using propane as a reductant under the condition of lean-burning exhaust [11]. However, the reason for the high activity and selectivity is not yet understood. In this paper, Co-Beta catalysts having various ion exchange levels and SiO_2/Al_2O_3 ratios are investigated. Results of catalytic activity tests are combined with Raman spectroscopic data to clarify the nature of active sites and their role in HC-SCR reaction.

2. Experimental

2.1. Catalyst preparation

Beta zeolites having various SiO_2/Al_2O_3 ratios were prepared according to patent literature [12]. Cobalt was loaded on Na or H-form Beta by ion exchange using a cobalt acetate solution at 60°C for 5 to 18 h. The ion exchange procedure was repeated several times to obtain the required cobalt loading. The ion-exchanged zeolites were filtered, washed, and dried at 110°C for 5 h, followed by calcination in air at 500 or 550°C. The resultant Co-Beta samples were pressed into pellets, crushed, and sieved to 1–2 mm granulates. Cobalt content was determined by inductively-coupled plasma atomic emission spectrometry, and ion exchange levels were calculated, assuming that one divalent cobalt ion is exchanged for two monovalent cations such as Na^+ or H^+. Hereafter, abbreviations such as Co-Beta(22.3, 80%) will be used, where the two parameters 22.3 and 80% denote the SiO_2/Al_2O_3 ratio of the zeolite and the ion exchange level, respectively. Samples with SiO_2/Al_2O_3 ratios ranging from 18 to 73 and ion exchange levels ranging from 46 to 110% were prepared by the procedure described above. One exception is Co-Beta(22.3, 132%), which was prepared by impregnation using cobalt acetate on Co-Beta(22.3, 80%). XRD analysis of the impregnated sample showed no peaks for Co_3O_4 spinel.

2.2. *Catalytic activity measurement*

Catalytic activity was measured in a fixed-bed flow reactor made of stainless steel (i.d. 14 mm). Typically, a 4 ml sample was used. The test gases were generated by mixing He-balanced standard gases using mass flow controllers. Water was added through a vaporizer before it entered the reactor. The gas composition at the outlet of the reactor was analyzed by a gas chromatograph and a chemiluminescence NOx analyzer equipped with an NO_2 converter. NOx and C_3H_8 conversions were defined as $2 \times (\text{evolved } N_2)/(\text{inlet NOx})$ and $(\text{inlet } C_3H_8 - \text{outlet } C_3H_8)/(\text{inlet } C_3H_8)$, respectively.

2.3. *Raman measurement*

Raman spectra were measured in air in back-scattering configuration by using 514.5 nm radiation from an argon ion laser (Coherent Innova 300) and a triple polychromator (Spex 1877) equipped with a CCD detector (Princeton Instruments LN-CCD 1100 PF/UV). The samples were pretreated by calcinating in air at 500°C for 9 h.

3. Results

3.1. *C_3H_8-SCR activity*

The HC-SCR activity of Co-Beta samples having different SiO_2/Al_2O_3 ratios and ion exchange levels are shown in table 1. The reaction conditions containing 10% oxygen and 9% water vapor, simulate the exhaust from a lean-burning gas engine operated at an air/fuel stoichiometric ratio (λ) of 2 except for NOx and C_3H_8 concentrations. On samples with low cobalt content such as Co-Beta(22.3, 46%) and (73, 106%), C_3H_8 conversion does not reach 100% even at 500°C, and NOx conversion is mainly determined by the reaction rate up to this temperature. On the other hand, with samples with higher cobalt contents, NOx conversion reaches a maximum below 500°C and decreases at higher temperatures. Almost 100% C_3H_8 conversion implies that NOx conversion is determined by the selectivity for NOx reduction rather than the reaction rate at these temperatures. Compared at the same SiO_2/Al_2O_3 ratio of 22.3, NOx conversion increases with an increase in the ion exchange level up to 80% while maintaining NOx reduction selectivity. However, further increase in the ion exchange level decreases NOx conversion especially at high temperatures. Besides, C_3H_8 conversion increases in spite of the decrease in NOx conversion. Clearly, selectivity for NOx reduction decreases. This suggests that the increase in ion exchange level does not necessarily mean an increase in the amount of the same active sites.

Activity tests were also performed at lower NOx and C_3H_8 concentrations. The results are shown in table 2. In this case, a significant decrease in both NOx and C_3H_8 conversions compared with those in table 1 is observed on low cobalt loading samples such as Co-Beta(22.3, 80%) and (44.1, 110%), whereas NOx conversion is not much reduced or even increases on samples with higher cobalt loading such as Co-Beta(22.3, 104%) and (17.9, 108%). Under these conditions, Co-Beta(22.3, 104%) shows the highest NOx conversion among samples with the same SiO_2/Al_2O_3 ratio. Co-Beta(22.3, 132%) shows lower NOx conversion compared with Co-Beta(22.3, 104%), and its selectivity for NOx reduction is apparently lower than those of samples with lower cobalt loadings. This also suggests the different nature of active sites on these samples.

3.2. *C_3H_8 oxidation activity*

To clarify the difference in selectivity, C_3H_8 oxidation activity in the absence of NOx was measured on Co-

Table 1
C_3H_8-SCR activity of Co-Beta [a]

SiO_2/Al_2O_3 ratio	Co loading (wt%)	Ion exchange level (%)	NOx (C_3H_8) conversion (%)			
			350°C	400°C	450°C	500°C
22.3	1.7	46		12.1 (11.2)		45.9 (51.7)
22.3	2.6	70		58.1 (61.6)		73.8 (83.7)
22.3	3.0	80	56.3 (57.2)	83.7 (94.7)	89.6 (97.9)	86.0 (99.8)
22.3	3.7	104	53.8 (73.7)	75.7 (96.4)	82.5 (99.1)	75.7 (99.8)
22.3	4.9	132	46.7 (84.2)	65.0 (97.0)	72.2 (99.6)	66.6 (100)
73	1.25	106		42.6 (56.8)		62.4 (96.7)
44.1	2.2	110	66.7 (99.4)	83.4 (99.8)	84.2 (100)	73.4 (100)
17.9	4.9	108	70.9 (89.4)	86.4 (97.6)	85.4 (99.2)	73.4 (100)

[a] Reaction conditions: NO 500 ppm, C_3H_8 1000 ppm, CO 1000 ppm, H_2 660 ppm, O_2 10%, CO_2 6%, H_2O 9%, GHSV 15000 h^{-1}.

Table 2
C_3H_8-SCR activity of Co-Beta (low concentration conditions) [a]

SiO_2/Al_2O_3 ratio	Co loading (wt%)	Ion exchange level (%)	NOx (C_3H_8) conversion (%)			
			350°C	400°C	450°C	500°C
22.3	3.0	80	46.8 (54.8)	70.0 (69.4)	72.4 (80.0)	71.9 (96.8)
22.3	3.7	104	76.1 (82.8)	82.5 (90.8)	76.1 (98.4)	60.9 (100)
22.3	4.9	132	55.7 (80.4)	75.7 (98.6)	75.3 (100)	64.2 (100)
44.1	2.2	110	28.2 (28.0)	60.7 (60.8)	72.0 (79.0)	73.4 (97.2)
17.9	4.9	108	71.4 (74.6)	82.3 (78.0)	83.4 (92.8)	71.9 (100)

[a] Reaction conditions: NO 150 ppm, C_3H_8 500 ppm, CO 1000 ppm, H_2 660 ppm, O_2 10%, CO_2 6%, H_2O 9%, GHSV 15000 h^{-1}.

Beta(22.3, 80%) and (22.3, 132%). The results are shown in table 3. At 450°C, C_3H_8 conversion is 72% on Co-Beta(22.3, 80%) and 93% on (22.3, 132%). This indicates that C_3H_8 oxidation by oxygen significantly affects NOx conversion at temperatures higher than 450°C. Comparing these data with the C_3H_8-SCR data in table 1, the following points are noticed: (i) C_3H_8 conversion shifts to lower temperature by ca. 100°C by the presence of NO, and (ii) at 500°C, C_3H_8 conversion by combustion reaches 98% or higher, indicating the severe competition of C_3H_8 combustion with NOx reduction. Further, it should be noted here that the C_3H_8 oxidation activity of Co-Beta(22.3, 132%) is higher than that of Co-Beta(22.3, 80%).

3.3. Comparison of NO and NO_2 as inlet NOx sources in C_3H_8-SCR

To clarify the role of NO_2 in HC-SCR, similar experiments were performed for NO and NO_2 in the presence and absence of C_3H_8. Table 4 shows a comparison of C_3H_8-SCR activity using NO or NO_2 in the feed. In this case, CO and H_2 were removed from the feed since they contribute to NO_2 reduction to NO. On both Co-Beta(22.3, 80%) and (22.3, 132%), the NOx conversion is significantly higher when NO is used in the feed, whereas the C_3H_8 conversion is higher when NO_2 is used under these conditions. Clearly, selectivity for NOx reduction is lower when NO_2 is used. The difference is more pronounced at lower temperatures. The NO_2 ratio as defined by $(NO_2)/(NO + NO_2)$ at the outlet of the reactor is shown in table 5. Experiments without C_3H_8 show the activity for the $NO + \frac{1}{2}O_2 \rightleftharpoons NO_2$ reaction. Whereas the equilibrium is attained at as low as 500°C on Co-Beta(22.3, 132%), the ratio is far from the equilibrium value even at 500°C on Co-Beta(22.3, 80%). This means that Co-Beta(22.3, 132%) has much higher NO oxidation (or NO_2 decomposition to NO and oxygen) activity than Co-Beta(22.3, 80%).

Table 3
C_3H_8 oxidation activity on Co-Beta [a]

Sample	C_3H_8 conversion (%)			
	350°C	400°C	450°C	500°C
Co-Beta(22.3, 80%)	3.3	18.9	72.1	98.0
Co-Beta(22.3, 132%)	8.2	30.9	93.4	100.0

[a] Reaction conditions: C_3H_8 1000 ppm, O_2 10%, H_2O 9%, GHSV 15000 h^{-1}.

In the presence of C_3H_8, i.e. under HC-SCR reaction conditions, the NO_2 ratio is far less than the equilibrium value even when NO_2 is used in the feed, showing the rapid reduction of NO_2 to NO in SCR reaction as already reported on Cu-ZSM-5 [13]. However, it is noticed that the NO_2 ratio is much higher on Co-Beta(22.3, 132%) than on Co-Beta(22.3, 80%) above 400°C, showing the fast NO oxidation on Co-Beta(22.3, 132%) competing with the fast NO_2 reduction under SCR conditions.

The above situation is almost the same in the low concentration conditions shown in table 6. However, the differences in NOx conversions between the case of NO and NO_2 are much smaller. It should be noted here that the NOx/C_3H_8 ratio is smaller (0.3) compared with the value in table 4 (0.5).

3.4. Raman measurement

Raman spectra of Co-Beta samples having the same SiO_2/Al_2O_3 ratio and various ion exchange levels are shown in figure 1 with those of parent Na-Beta and Co_3O_4 spinel. The spectra of Co-Beta(22.3, 70%) and (22.3, 80%) closely resemble that of Na-Beta. This suggests that cobalt is well-dispersed and oxide phase is not present on these samples. Whereas, in the spectrum of Co-Beta(22.3, 132%), in addition to the bands of zeolite framework, sharp bands are observed at 691 and 524 cm^{-1}. Although a broad and weak band originating from zeolite framework is observed at around 690 cm^{-1} on other Beta samples, the 691 cm^{-1} band of Co-Beta(22.3, 132%) is distinguished because of its intensity and sharp band form. As the position and the pattern closely resemble those of Co_3O_4, these are assigned to Co_3O_4 oxide spinel. This indicates that on Co-Beta(22.3, 132%), loaded cobalt is agglomerated to form cobalt oxide spinel phase. Further, it is notable that in the spectrum of Co-Beta(22.3, 104%) having intermediate cobalt

Table 4
C_3H_8-SCR activity on Co-Beta: comparison of NO and NO_2 [a]

Sample	Inlet condition	NOx (C_3H_8) conversion (%)			
		350°C	400°C	450°C	500°C
Co-Beta(22.3, 80%)	$NO + C_3H_8$	61.6 (79.4)	81.6 (98.6)	87.0 (99.7)	75.7 (100)
	$NO_2 + C_3H_8$	50.7 (87.7)	71.3 (99.3)	80.5 (100)	68.4 (100)
Co-Beta(22.3, 132%)	$NO + C_3H_8$	55.3 (87.0)	65.9 (99.6)	70.6 (100)	61.5 (100)
	$NO_2 + C_3H_8$	43.6 (92.4)	57.5 (99.7)	63.8 (100)	52.2 (100)

[a] Reaction conditions: NO or NO_2 500 ppm, C_3H_8 1000 ppm, O_2 10%, H_2O 9%, GHSV 15000 h^{-1}.

loading, a broad and strong band is observed around 600 cm^{-1}. As this band is not observed on Na-Beta nor Co_3O_4, it is considered to be related with a state of loaded cobalt other than Co_3O_4.

4. Discussion

Table 1 shows that NOx conversion increases with an increase in the ion exchange level below 100% while maintaining the selectivity for NOx reduction. This implies that the same active site increases with an increase in the ion exchange level. Raman results suggest this active site is mono-atomically or at least well-dispersed cobalt, although no direct information on the species is observed. Since samples with ion exchange levels below 100% keep high NOx reduction selectivity up to a high temperature of 500°C, this well-dispersed cobalt is considered to have high selectivity for NOx reduction. A slight decrease in NOx conversion is observed on Co-Beta(22.3, 80%) at 500°C compared with that at 450°C. This is considered to be due to the decrease in selectivity caused by C_3H_8 oxidation by oxygen. The C_3H_8 oxidation results in table 3 support this consideration.

It is noticed that the increase in NOx conversion at 400°C from 12 to 84% with an increase in the ion exchange level from 46 to 80% is not in linear dependency. Similar results are reported for CH_4-SCR on Co-ferrierite by Li and Armor [14]. One explanation is that there exist several different ion-exchangeable sites with different energy stabilities and NOx reduction activities. However, in the case of Beta having pores of almost the same diameter (12-membered ring) in two directions, it is difficult to consider that there exists an ion exchangeable site to which it is difficult for reactants to access. Another explanation is the promotion by the neighboring sites. Considering that at least three molecules, i.e. two NOx molecules and one C_3H_8 molecule, must be involved to produce N_2, it would be important to adsorb many molecules in the proximity, and therefore positive effect of neighboring sites would be reasonable.

When the ion exchange level exceeds 100%, decrease in selectivity is observed especially at high temperatures. Raman spectra show the presence of Co_3O_4 spinel phase in Co-Beta(22.3, 132%). It is well known that Co_3O_4 spinel has high activity for hydrocarbon oxidation, and hydrocarbon oxidation by oxygen on cobalt oxide is considered to occur. Further, the TPD spectrum of Co-Beta with an ion exchange level much higher than 100% (Co-Beta(17.5, 126%)) shows a peak above 600°C, indicating the presence of dissociatively adsorbed oxygen [15]. C_3H_8 oxidation results in table 3, which shows the higher C_3H_8 oxidation activity than that of Co-Beta(22.3, 80%), supports this consideration.

Samples with different SiO_2/Al_2O_3 ratios show similar features of activity. Co-Beta(17.9, 108%) and (44.1, 110%) shows similar activities to those of Co-Beta(22.3, 104%) under the conditions in table 1. Under the conditions in table 2, Co-Beta(44.1, 110%) shows quite lower conversions below 400°C than those of Co-Beta(22.3,

Table 5
$NO_2/(NO + NO_2)$ ratio in C_3H_8-SCR on Co-Beta [a]

Sample	Inlet condition	$NO_2/(NO + NO_2)$ ratio (%)			
		350°C	400°C	450°C	500°C
Co-Beta(22.3, 80%)	NO	5	7	11	16
	NO_2	83	80	71	50
	$NO_2 + C_3H_8$	39	14	2	10
Co-Beta(22.3, 132%)	NO	17	29	32	27
	NO_2	82	65	44	28
	$NO_2 + C_3H_8$	31	21	17	17
none (blank)	NO	3	9	10	15
	NO_2	94	93	89	74

[a] Reaction conditions: NO or NO_2 500 ppm, C_3H_8 0 or 1000 ppm, O_2 10%, H_2O 9%, GHSV 15000 h^{-1}.

Table 6

C_3H_8-SCR activity on Co-Beta: comparison of NO and NO_2 (low concentration conditions) [a]

Sample	Inlet condition	NOx (C_3H_8) conversion (%)			
		350°C	400°C	450°C	500°C
Co-Beta(22.3, 80%)	NO + C_3H_8	51.6 (67.2)	72.8 (71.4)	72.7 (81.4)	69.2 (98.6)
	NO_2 + C_3H_8	44.5 (71.3)	71.0 (77.9)	71.9 (85.8)	67.7 (98.9)
Co-Beta(22.3, 132%)	NO + C_3H_8	48.1 (90.4)	75.2 (98.3)	75.5 (100)	56.4 (100)
	NO_2 + C_3H_8	43.4 (91.7)	70.4 (98.9)	71.6 (100)	53.1 (100)

[a] Reaction conditions: NO or NO_2 150 ppm, C_3H_8 500 ppm, O_2 10%, H_2O 9%, GHSV 15000 h^{-1}.

104%), but it is merely because the reaction is mainly rate-determined owing to its low cobalt content. Further discussions will not be made here, since comparison of different SiO_2/Al_2O_3 ratio samples requires the use of different parent Beta, and to control the zeolite crystallinity and particle size would be required for accurate comparison.

It has been a matter of question whether NOx or oxygen activates the hydrocarbon in HC-SCR reaction [5,6,16–18]. In C_3H_8-SCR on Co-Beta, the hydrocarbon conversion temperature is shifted to a lower temperature by ca. 100°C in the presence of NOx, and simple oxidation of reductant is minimal at a reaction temperature around 400°C. Therefore, NOx rather than oxygen seems to activate C_3H_8.

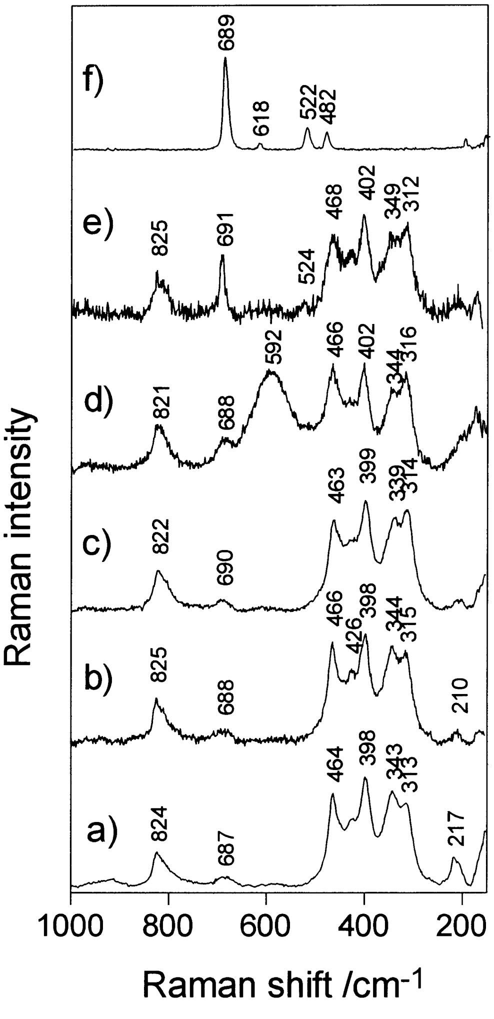

Figure 1. Raman spectra of Co-Beta. (a) Na-Beta, (b) Co-Beta(22.3, 70%), (c) Co-Beta(22.3, 80%), (d) Co-Beta(22.3, 104%), (e) Co-Beta(22.3, 132%), (f) Co_3O_4.

The role of NO_2 in HC-SCR reaction has also been discussed. It is reported that NO oxidation to NO_2 is the initial step of NO reduction on H- [19], Cu- [16] and Co- [20,21] zeolites. Further, Misono et al. reported the promotion of SCR by C_3H_6 on Ce-ZSM-5 by the addition of CeO_2 and ascribed the effect to the NO oxidation to NO_2 on CeO_2 [22]. However, in C_3H_8-SCR on Co-Beta no promotion effect was seen when NO_2 was used in the feed both in the case of Co-Beta(22.3, 80%) and (22.3, 132%), although the C_3H_8 conversion becomes higher under the present experimental condition. Besides, on Co-Beta(22.3, 132%), although the NO_2 concentration is kept much higher compared with the case of Co-Beta(22.3, 80%) owing to the high NO oxidation activity by the Co_3O_4, the NOx conversion is significantly lower while the C_3H_8 conversion is higher under the conditions of table 1. At temperatures below 400°C, the effect of C_3H_8 oxidation by oxygen is not so great as shown in table 3. These results suggest that the decrease in selectivity is caused by NO_2 or to be accurate, the high NO_2 ratio to total NOx. One explanation is the consumption of the hydrocarbon by NO_2 to form NO. Considering the competition of this reaction and NOx reduction to N_2, it is well explained that the C_3H_8 conversion is constantly higher in the case of NO_2 and that the difference in NOx conversion between the cases of NO and NO_2 is smaller at relatively low NOx/C_3H_8 ratios (table 6). Such a reaction of NO_2 with hydrocarbon to form NO is already reported on Cu-ZSM-5 [13] and low NO_2 ratios in the SCR outlet gas shown in table 4 suggest that the same reaction proceeds on Co-Beta.

Contrary to previous studies, in C_3H_8-SCR on Co-Beta in this study, no promotion effect was found when NO_2 was used in place of NO. One explanation is the following. Armor et al. proposed the reaction scheme for CH_4-SCR on Co-ferrierite in which NO_2 adsorbed on Co is regenerated after it has activated CH_4 [20]. In this case, although NO_2 is involved in the reaction, it is required only in catalytic amount rather than in stoichiometric amount. It seems that since Co-Beta can efficiently form and support such adsorbed NO_2 on active centers, there is no need for excess amount of gas-phase NO_2. After all, stoichiometric amount of NO_2 in the gas phase is not required for C_3H_8-SCR on Co-Beta.

Quite interesting is the high activity of Co-Beta(22.3, 104%) under low concentration conditions in table 2. From Raman data, an intermediate state of loaded cobalt between well-dispersed phase and oxide phase, such as dimer, as already reported on Cu-ZSM-5 [23] is suggested. Such loaded state may contribute to high activity and selectivity for NOx reduction. However, further experiments would be required to discuss the origin of the band and its role in catalytic activity.

5. Conclusions

In the HC-SCR reaction on Co-Beta using propane as a reductant, highly-dispersed cobalt is essential for the high activity and selectivity for NOx reduction. NOx reduction activity increases with an increase in the cobalt ion exchange level below 100% while maintaining NOx reduction selectivity. At high ($\gg 100\%$) cobalt loading, the presence of cobalt oxide (Co_3O_4) phase is observed by Raman spectroscopy. This phase promotes hydrocarbon oxidation by oxygen, thus lowering the selectivity. At the cobalt loading around 100%, another active site appears and shows high activity especially at low NOx concentrations. Concerning the role of NO_2 in NOx reduction, gas-phase NO_2 is not required in stoichiometric amount, and too much NO_2 in the gas phase decreases the selectivity for NOx reduction since reduction of NO_2 by hydrocarbon to form NO proceeds and competitively consumes the reductant.

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